

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2523

ROTOGENERATIVE DETECTION OF CORROSION CURRENTS

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Armour Research Foundation



Washington

November 1951

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SUMMARY

A new technique for studying corrosion phenomena is described. The method permits the detection of the presence of currents produced by local cells on the surface of a corroding metal specimen. The principle employed is as follows: A cylindrical specimen is rotated at several hundred revolutions per minute in the corrosion medium. A small reference electrode is positioned as near the specimen as possible, thus scanning the surface of the metal. The signal produced is amplified and applied to an oscilloscope, together with a suitably synchronized sweep voltage. Thus, there is produced on the oscilloscope a standing pattern which is a reproduction of the potential fields set up in the corrosion medium by the currents flowing between the elements of local cells.

The method can be applied to the study of stress corrosion; in this case a hollow specimen is subjected to sufficient hydraulic pressure to produce the desired stress level. Other fields in which the equipment may be of value are: Inhibitor action, cathodic protection, and general corrosion phenomena.

INTRODUCTION

The generally accepted electrochemical theory of corrosion states that certain areas of a corroding metal surface behave as anodes, while the remaining areas function as cathodes; the combination of two such electrodes produces a "corrosion cell." The current flowing in this cell may be called "local action" when a single metal is involved, or "galvanic action" when dissimilar metals are present.

The dimensions of such corrosion cells vary widely. Uniform general attack indicates close spacing of cell elements; nonuniform or "pit-type" corrosion indicates appreciable separation between anodic centers.

The potential differences which give rise to corrosion currents may originate from a great many sources. These include dissimilar metals, nonhomogeneity in a single metal, and variations in the composition of the corrosion medium.

The magnitude of the corrosion current flowing in a given corrosion couple depends on several factors including the potential which drives the cell, the resistance of the electrolyte, and a number of complex physical and chemical properties of the system which are lumped under the heading "polarization characteristics."

Whatever the cause or magnitude of the currents which attend corrosion phenomena, a need has long been felt for better methods of detecting, measuring, and locating these currents during the actual corrosion process.

In theory, it is possible to trace out the equipotential lines (and lines of current flow) in any electrolytic medium merely by exploring the solution in the vicinity of the corrosion cell with one or more reference electrodes and a potentiometer. This technique has been applied to a number of experimental corrosion couples with some success. For example, Copson (reference 1) investigated the potential field surrounding a nickel-iron corrosion couple in tap water and successfully correlated the galvanic current with the observed corrosion, both as to magnitude and distribution. Similarly, Akimov and Golubev (reference 2) explored the potential fields surrounding model corrosion couples having various geometric arrangements. In both these examples, however, the corrosion cells used had rather large dimensions and the corrosion media were not highly conductive. The voltages to be detected were therefore reasonably large and could be measured readily with conventional direct-current instruments.

A somewhat different approach was used by Dix (reference 3), who isolated regions of the corrosion specimen suspected of being anodic or cathodic and measured the open-circuit solution potential of each in turn. Thus, he was able to identify the corrosion cell components and locate them on the specimen surface. By coupling two identical specimens, one of which had exposed anodic areas and the other exposed cathodic areas, he could simulate the corrosion process which would occur on uncoated specimens and measure the current flowing in the cell.

The purpose of this paper is to present a new method of detecting and locating local-action currents during corrosion. It can be used with electrolytes varying widely in conductivity and is applicable to systems whose local cells have rather small physical dimensions. Its principal advantage over the other methods described above is that corrosion currents can be detected even when the precise location of

anodic and cathodic areas is not known beforehand, provided the corrosion currents produce a potential field around the tip of the electrode.

The work described herein was carried out under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics and was part of a project directed toward a fundamental study of the stress corrosion of aircraft alloys.

DEVELOPMENT OF THE ROTOGENERATIVE METHOD

As mentioned above, one may scan the surface of a corroding metal, using a reference electrode to detect variations in the potential of the electrolyte. Those regions of the electrolyte near cathodic zones of the specimen will be relatively more negative than those near anodic zones. While this technique is theoretically applicable to any corroding metal, in most cases the magnitude of the potential difference which must be detected is very small compared with the corroding potential of the specimen as a whole. Moreover, the corroding potential of a metal specimen is rarely sufficiently constant to admit of high-precision measurement. Consequently, direct-current scanning of a corroding metal surface (at least in a high-conductivity medium) is difficult if not impractical.

On the other hand, if it were possible to separate the small (IR) potential drop produced by the corrosion current from the potential of the specimen as a whole, detection of these currents would be greatly simplified.

Such separation can be accomplished through the use of a rotating cylindrical specimen, scanned by a fixed reference electrode located close to the surface of the corroding metal. This technique in effect "generates" an alternating-current signal which is a reproduction of the potential gradients set up in the corrosion medium by the local-action currents - hence the name "rotogenerative." The direct-current potential of the specimen as a whole is readily blocked by a series capacitance, permitting amplification of the alternating-current component to the desired level.

Using this technique, it is not necessary that the corroding potential be constant; a gradual drift of the direct-current potential of the specimen will not be detected by the amplifier system. The alternating-current signal, however, is passed readily by the condenser when rotational speeds of several hundred revolutions per minute are used.

APPARATUS

A schematic diagram of the complete rotogenerative apparatus is shown in figure 1. An electric motor rotates the cylindrical corrosion specimen at 1725 rpm. A group of reference or scanning electrodes (silver wires mounted in an insulating support) is positioned close to the corroding metal surface. The alternating-current component of the signal from a selected scanning electrode is fed to an amplifier through a 1-microfarad condenser. The amplified signal actuates the vertical deflection plates of an oscilloscope. The sensitivity of the system is about 1 millivolt per inch on the oscilloscope screen.

Horizontal sweep voltage is provided by an "angular sweep potentiometer,"¹ which is gear-driven at the same speed as the specimen. Thus, perfect synchronization of the vertical and horizontal signals is assured. Under steady-state conditions the distribution of anodic and cathodic zones may be observed directly on the oscilloscope screen in the form of a complex standing wave. A record of the oscilloscope pattern may be made at any time by means of an electrically operated, 16-millimeter, single-frame camera. Using a shutter speed of about 1/30 second, single oscilloscope traces are recorded.

For investigation of stress-corrosion phenomena, a hollow cylindrical specimen is used. Internal hydraulic oil pressure provides the desired stress level in the walls of the (rotating) specimen. The circumferential tensile stress in the outer surface of the cylinder can be calculated readily from the internal pressure.

Figure 2 shows the apparatus in readiness for operation. The specimen extends below the main platform of the apparatus into the corrosion medium, which is contained in the glass vessel. The sweep generator is visible in the upper right; its direct-current amplifier is in the background. The other components are identified in the figure legend.

RESULTS

In order to test the theory of operation of the method described above, a "synthetic" corrosion specimen was devised and scanned by the apparatus. This specimen (fig. 3) was made from mild steel. Twenty vertical lines were scribed on the cylindrical surface at equal intervals around the disk. The specimen was then silver-plated and

¹Manufactured by Rowe Radio Res. Lab. Co., Chicago, Ill.

rescribed to expose thin lines of steel at each reference mark. The disk was mounted on a rod which was held in the rotating apparatus.

The disk was immersed in dilute hydrochloric acid and scanned, using a silver wire reference electrode. The pattern obtained is shown in figure 4. The polarity of the amplifier and oscilloscope connections was such that the upward pips of the pattern represent anodic regions of the specimen (exposed steel), while the downward portions of the pattern correspond to the cathodic (silver) areas. It will be noted that only 19 anodic pips are present in the oscilloscope trace; the other is visible within the "fly-back" region of the sweep generator.

It is also apparent from figure 4 that all of the exposed steel areas do not show equal anodic action; this is probably due to variation in the area of steel exposed at the several scratch lines. The oscilloscope pattern produced, however, indicates that a picture of the distribution of corrosion currents is obtained and hence of the corrosion itself, over the specimen surface.

In order to check the correlation between the position of the anodic pips in figure 4 and the actual position of each scribe mark on the disk, the trace of figure 4 was measured with a comparator microscope and the results plotted in figure 5. It is apparent that the linearity of the over-all horizontal scanning system is reasonably good.

The above data illustrate the application of the rotogenerative technique to a corroding system having known dimensions and electrochemical properties. Its principal utility, of course, should lie in the investigation of the corrosion of metals and alloys in which the disposition of anodic and cathodic areas is unknown. Such a study is currently in progress, and involves the stress corrosion of certain aircraft alloys.

While the results of this study are not sufficiently complete to justify their detailed presentation at this time, some representative oscilloscope traces will illustrate the nature of the data which are obtained.

The oscilloscope pattern shown in figure 6 was obtained during the corrosion of a medium-grain-size aluminum and 4 percent copper alloy in a sodium-chloride and hydrogen-peroxide solution. Figure 7 was obtained from a very large-grained alloy of similar composition immersed in a salt-peroxide solution to which sodium chromate had been added to reduce the rate of attack.

The complexity of the pattern of figure 6 reflects the severe attack which was in progress. The relative simplicity of figure 7 was correlated with the slight pitting-type attack observed in the chromate-inhibited medium.

Figures 6 and 7 are included merely to show the form of the oscilloscope patterns which are observed with the technique described. Interpretation of these and other data will be undertaken only when an adequate study of these alloys has been completed.

DISCUSSION

The basic assumption upon which the rotogenerative technique depends is that the electrostatic fields which are set up in the electrolyte by the corroding metal rotate with the specimen. It has been demonstrated experimentally that no appreciable "drag" effect exists at the rotational speeds used.

This conclusion is based on experiments performed during preliminary stages of the development. Several synthetic corrosion specimens were made by electroplating various metals on a 0.75-inch steel bar. Scratches were then put on the specimens to expose the base metal at selected spots. Upon scanning these specimens in various electrolytes, oscilloscope patterns were obtained which correlated with the known geometry of the local corrosion cells. The rotational speed used was varied from about 60 to about 1800 rpm; in no case did the speed change cause a shift in the position of the pattern on the oscilloscope screen.

Thus far, the rotogenerative technique has been applied only to stress-corrosion studies. It may have application in other electrochemical problems - for example, cathodic-protection, inhibitor-action, and electrodeposition studies.

The technique described appears to offer a new tool for the investigation of corrosion (and other electrochemical) phenomena. While it has not been attempted thus far to interpret quantitatively the vertical displacement of the oscilloscope traces (representing magnitudes of corrosion currents), it has been found possible with simple patterns to correlate the horizontal displacement with position of local anodes and cathodes. Further investigation should lead to a more complete understanding of the potentialities and limitations of the method.

REFERENCES

1. Copson, H. R.: Distribution of Galvanic Corrosion. Trans. Electrochem. Soc., vol. 84, 1943, pp. 71-82.
2. Akimov, G. V., and Golubev, A. I.: Investigation of the Corrosion Processes Using a Model of Local Galvanic Couples. Jour. Phys. Chem. (USSR), vol. 20, 1946, pp. 303-314.
3. Dix, E. H., Jr.: Acceleration of Rate of Corrosion by High Constant Stresses. Trans. Am. Inst. Min. and Met. Eng., vol. 137, 1940, pp. 11-40.

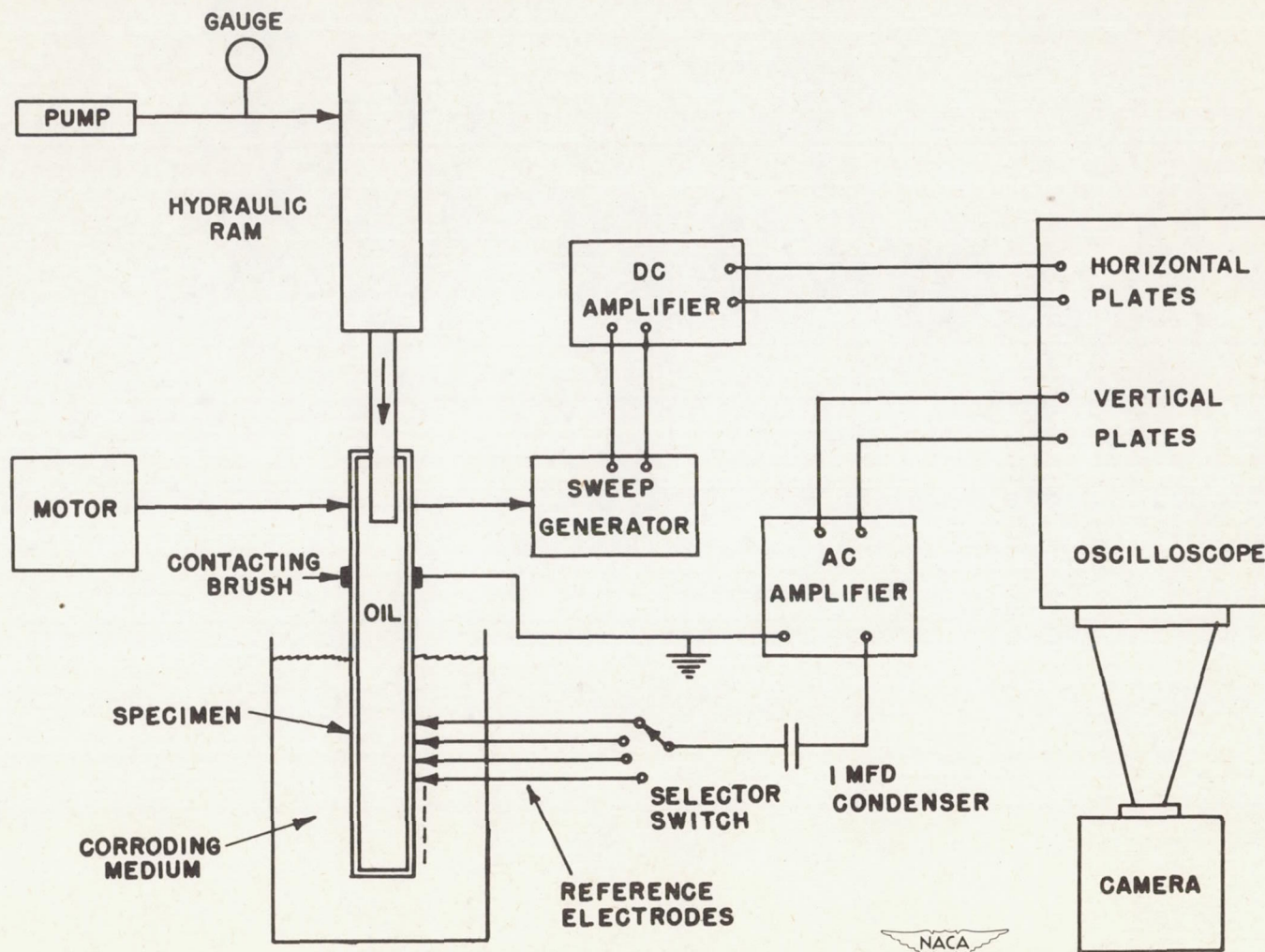


Figure 1.- Schematic diagram of rotogenerative apparatus.

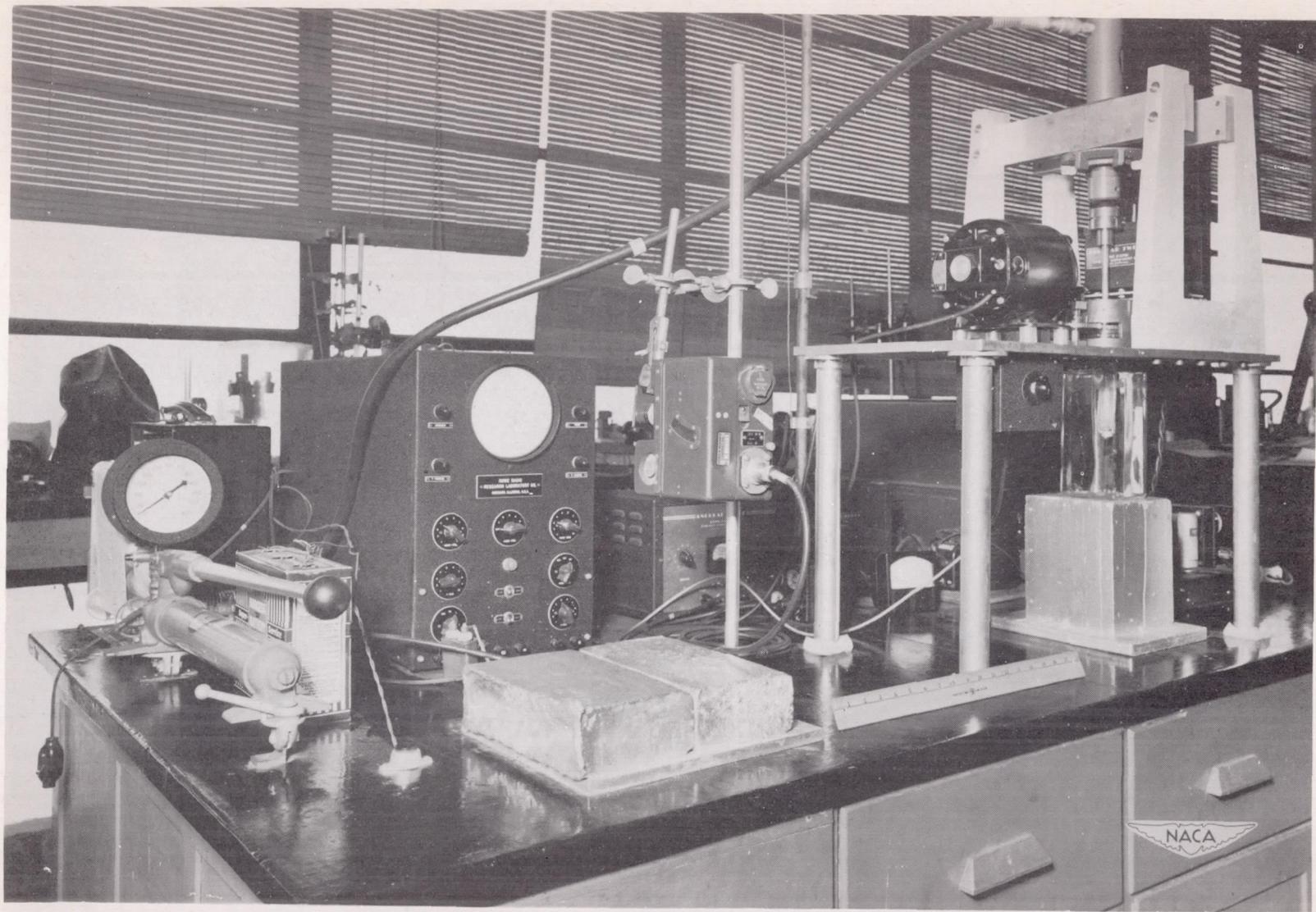


Figure 2.- Photograph of rotogenerative apparatus. At left, note hydraulic pump and gauge, oscilloscope, and camera; at right, note rotating mechanism, hydraulic ram, and corrosion medium.

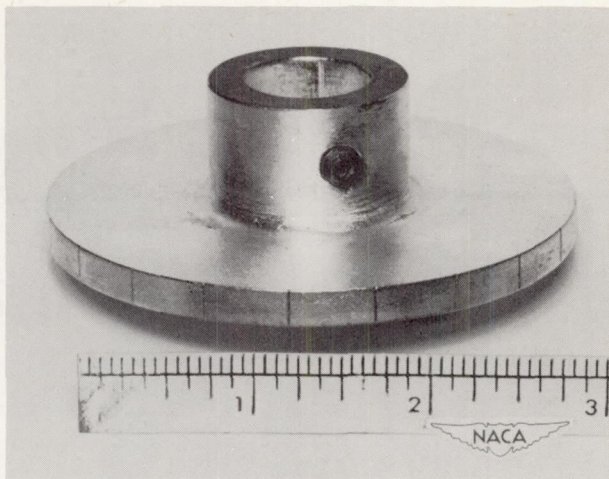


Figure 3.- Calibration disk.

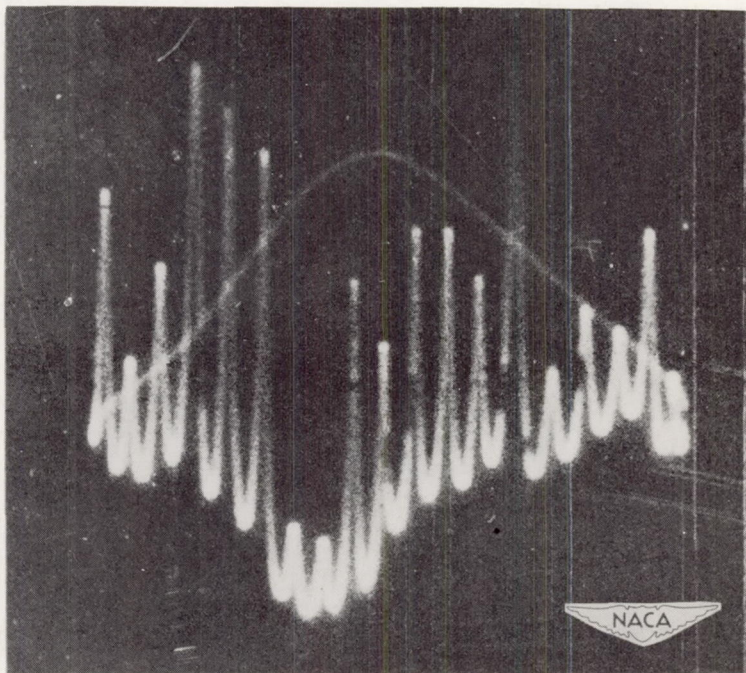


Figure 4.- Calibration trace.

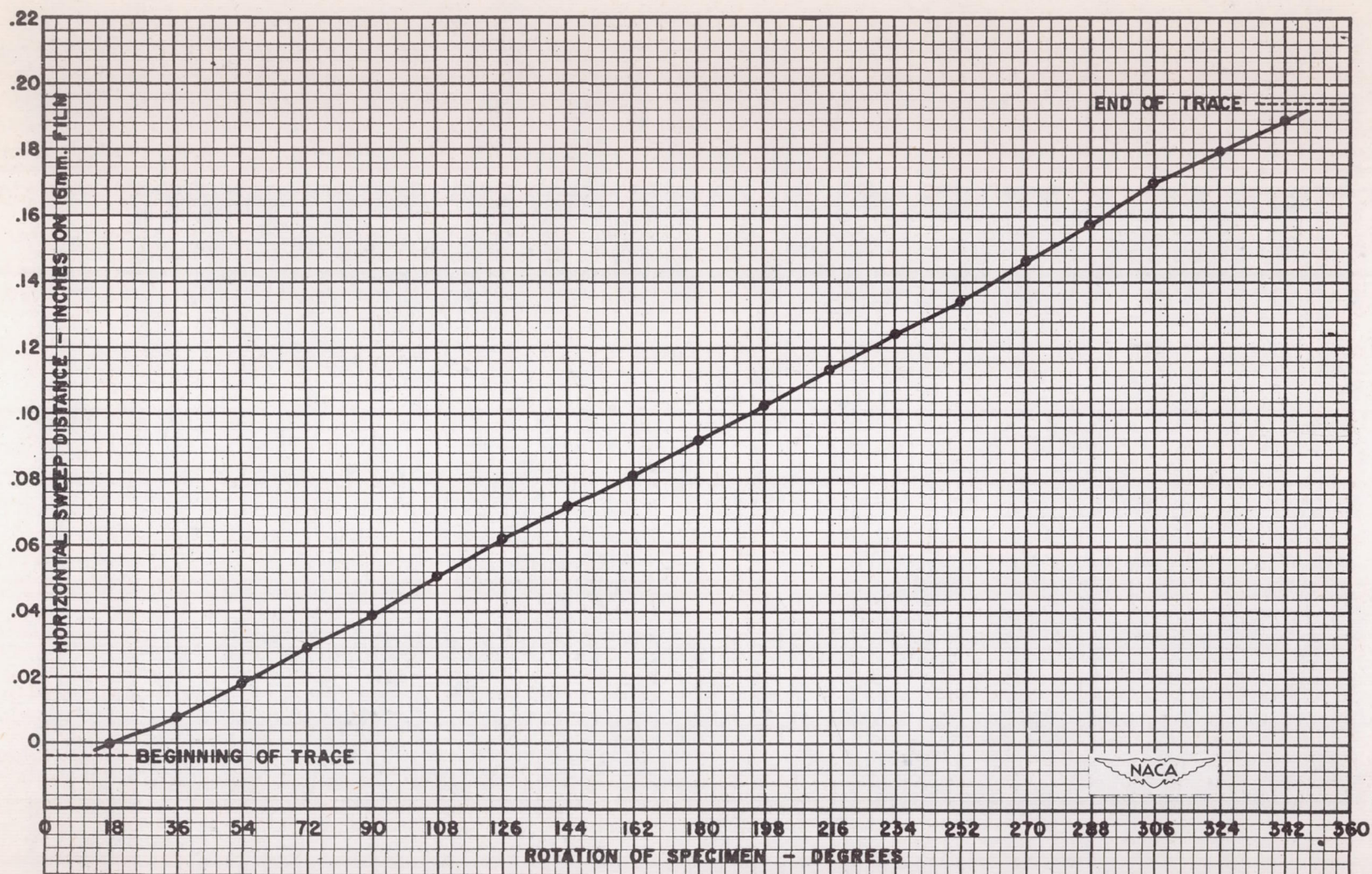


Figure 5.- Linearity of sweep generator.

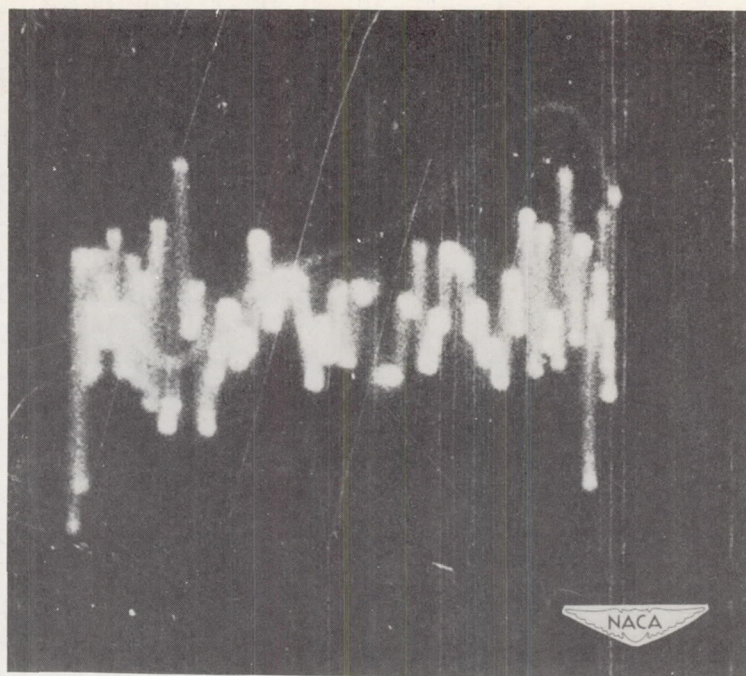


Figure 6.- Oscilloscope pattern of aluminum and 4 percent copper in a sodium-chloride and hydrogen-peroxide medium.

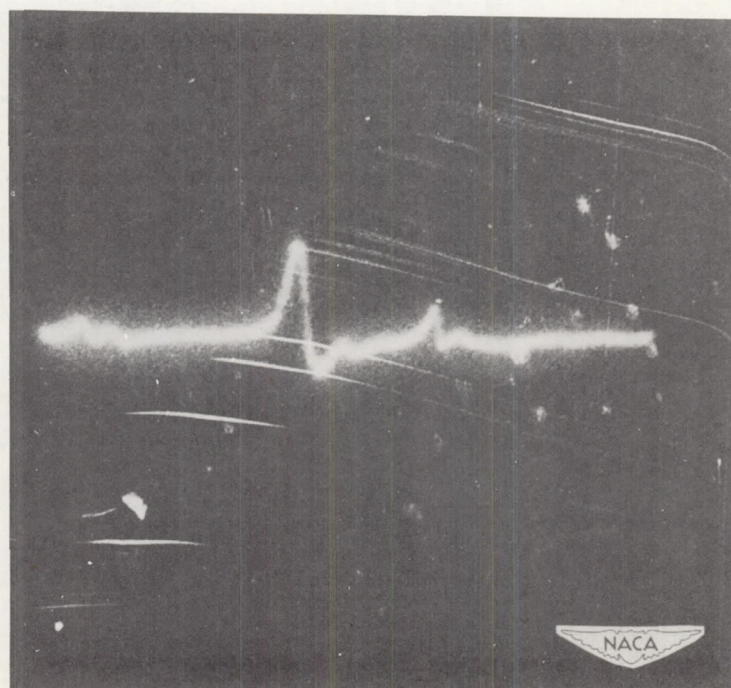


Figure 7.- Oscilloscope pattern of aluminum and 4 percent copper in a sodium-chromate-inhibited salt-peroxide solution.